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VIBRATIONAL SPECTROSCOPY OF SHOCK-COMPRESSED FLUID N_2 AND O_2 *

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Single-pulse, multiplex, coherent anti-Stokes Raman scattering (CARS) was used to observe the vibrational spectra of liquid N_2 shock-compressed to several pressures and temperatures up to 41 GPa and 5200 K and liquid O_2 shock-compressed to several pressures and temperatures up to 10 GPa and 1000 K. For N_2 , the experimental spectra were compared to synthetic spectra calculated using a semiclassical model for CARS intensities and estimated vibrational frequencies, peak Raman susceptibilities and Raman line widths. The question of excited state populations in the shock-compressed state is addressed.

Recently, the high-pressure, high-temperature behavior of N_2 and O_2 have received considerable attention. Several dynamic¹⁻⁴ and static⁵⁻⁹ experiments have produced equation-of-state and thermodynamic data for N_2 and O_2 at pressures up to 130 GPa and at elevated temperatures to beyond 10,000 K. These measurements have been complemented by calculations that describe the thermodynamic state of the solid¹⁰ or the fluid¹¹⁻¹⁴. An increase in compressibility along the N_2 Hugoniot at pressures above 30 GPa has been attributed^{10,11,14} to dissociation. The intramolecular stretching frequencies for solid N_2 ^{7,15} and solid O_2 ¹⁶ have been measured and calculated¹⁷ using a perturbation analysis in conjunction with appropriately chosen potential functions^{13,14}. Vibrational frequencies have also been measured for the fundamental and some excited state transitions of fluid N_2 at pressures and temperatures up to 34 GPa and 4400 K^{6,18}. Recently, N_2 vibrational frequencies have been calculated versus pressure and temperature.¹⁹ There have, however, been no measurements or calculations of the O_2 vibrational frequencies in the dense fluid state. Such results and higher pressure/temperature data for N_2 would be of value both

to characterize the potential functions of these molecules and possibly to observe the onset of dissociation. Measurements of ground and excited state vibrational transition intensities could also provide an upper limit estimate for dense-phase fluid vibrational relaxation times.²⁰

Reported here are coherent anti-Stokes Raman scattering (CARS) measurements of N_2 and O_2 shock-compressed to 41 GPa and 10 GPa, respectively. The pressure/temperature states were achieved by dynamic compression techniques using an experimental apparatus described previously.²¹ Briefly, a projectile launched by a two-stage light gas gun dynamically compressed a fluid N_2 or O_2 sample that had been condensed into a cryogenic target assembly. The target was designed to reflect CARS signals from a highly polished 304 stainless steel target plate at the front through a 63- μ m-diam quartz or lithium fluoride window at the rear. Single-shock velocities were conservatively measured to ± 0.2 km/sec and the initial pressure and temperature of the liquid sample were determined to ± 0.3 kPa and 11 K, respectively. Initial sample densities of N_2 and O_2 were taken from Jacobsen, et al.²² and Weber,²³ respectively. The samples were condensed from gaseous N_2

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(>99.9% purity) and gaseous O_2 (>99.6% purity)

CARS²⁴ occurs as a four-wave parametric process in which three waves, two at a pump frequency and one at a Stokes frequency, are mixed in a sample to produce a coherent beam at the anti-Stokes frequency. The efficiency of this mixing is greatly enhanced if the difference in frequencies between the pump and Stokes coincides with the frequency of a Raman active mode of the sample. A previously described¹⁶ semiclassical model was used to calculate synthetic CARS spectra that matched the experimental data. In these experiments, a Nd:YAG laser was used to pump the two dye lasers that generate the CARS signal, one being a broadband "Stokes" laser (630-650 nm) and the other a narrowband "pump" laser operated near 557 nm for N_2 experiments and near 582 nm for O_2 experiments. Multichannel detection of the CARS signals was done using an intensified photodiode array and analyzer. In addition, the broadband dye laser spectral profile was measured in each experiment using another spectrometer and photodiode array. Wavelength calibrations were all done using vacuum wavelengths of atomic emission lines.²⁵

Shock pressures and temperatures were calculated using an effective spherical potential that has been shown to reproduce accurately both nonspherical molecular dynamics simulations and experimental Hugoniot and brightness temperature data for N_2 .^{13,14} Taking into account the accuracy of the method for N_2 , and the similarity of potentials for N_2 and O_2 , an effective spherical potential for O_2 was fit directly⁴ to Hugoniot data³ and was checked by its good fit to reflected shock data.³ In this work, doubly shocked states are inferred from impedance matching of the initial shock at the measured shock velocity, reflecting off the known window material assuming the theoretical equation of state for N_2 and O_2 . The equation-of-state parameters for quartz and lithium

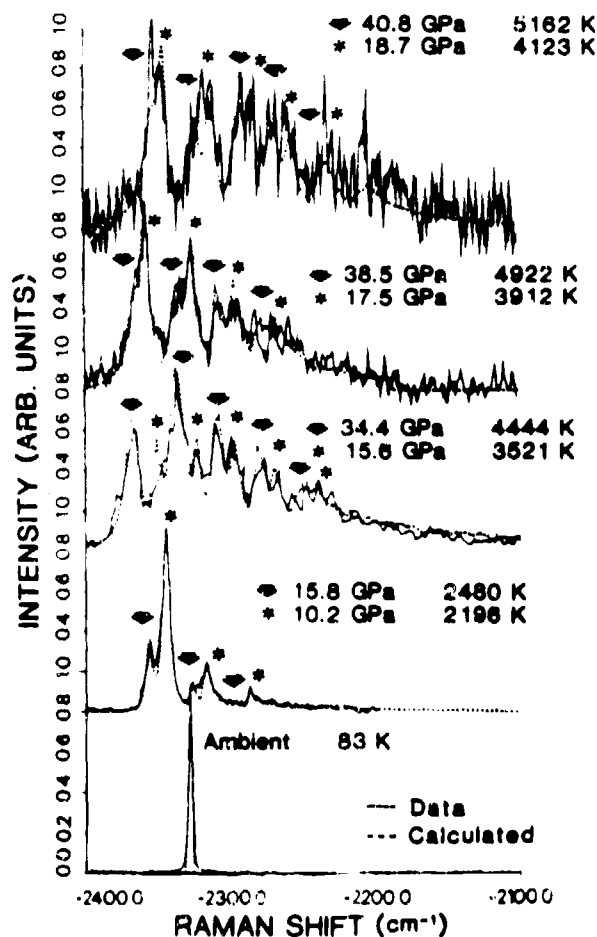


FIGURE 1
Experimental and computed CARS spectra of shock-compressed liquid N_2 .

fluoride are from published data.²⁶ Based on the previously stated experimental errors, estimated uncertainties in pressure are about ± 1 GPa for principal Hugoniot measurements and ± 2 GPa for reflected shocks. These uncertainties are dominated by the experimental uncertainty in the shock velocity. Temperature uncertainties are dominated by a systematic shift of up to 10% depending on the theoretical model chosen.^{12,14}

The observed single pulse CARS spectra of ambient pressure and eight (four experiments) dynamically compressed states of liquid N_2 are shown in Fig. 1. Also shown are preliminary synthetic spectra. Because of timing

constraints and the desire to have no shocked sample at the time the laser pulses arrived at the sample, the shockwave had reflected off of the rear window back into the sample producing a doubly shocked region. Spectral features from both the singly (denoted by asterisks) and doubly (arrows) shocked regions are clearly observed.

Previous observations by Reichlin et al.¹⁷ for solid N_2 show that the vibrational frequencies tend to first increase and then decrease with increasing pressure. Visual inspection of the data in Fig. 1 suggests that this also is the case at Hugoniot conditions only with the reversal occurring at much lower pressures. This behavior has been suggested by theoretical calculations.¹⁹ The data are presently being analyzed to obtain more accurate values for transition frequencies, line widths, and peak Raman susceptibilities. Previous work¹⁸ on the lower pressure data of Fig. 1 (0.2-15.8 GPa and 15-300 K) spectra has shown that vibrational equilibration among the thermally accessible levels occurs in <50 ns; we are presently doing similar calculations for the higher-pressure data.

The observed single-pulse CARS spectra of ambient pressure and five (four experiments; dynamically compressed states of liquid O_2 are shown in Fig. 2. For the higher-pressure data in these experiments, the CARS spectrum was obtained before the shock wave reached the target assembly window. Hence only the singly shocked (asterisks) and ambient-pressure (unlabeled) states are observed spectrally. We are presently analyzing these data using the semiclassical CARS intensity model. The visible absorption of O_2 that is due to van der Waals interaction- or collision-induced transitions¹⁶ could drastically influence the third-order susceptibility. In order to fully model the CARS spectra, it is therefore first necessary to measure the absorption in O_2 at the pressures

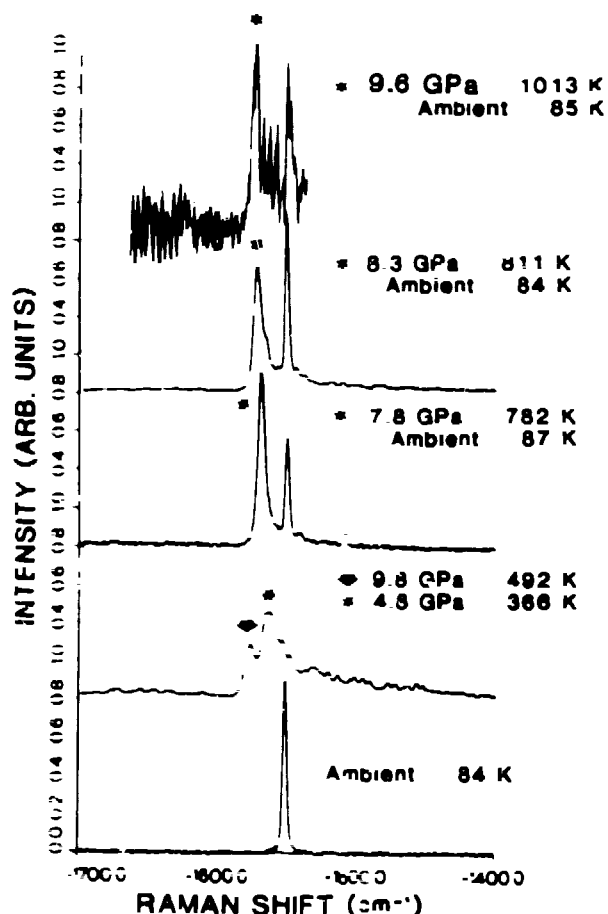


FIGURE 2
Experimental CARS spectra of shock-compressed liquid O_2 .

and temperatures of interest. Such measurements are in progress.

In summary, the vibrational transitions of N_2 and O_2 at pressures up to 41 GPa (3200 K) and 19 GPa (1800 K), respectively, have been measured. The data suggest that N_2 and O_2 still exist as molecular fluids at these pressures and temperatures. Visual inspection of the N_2 data suggests that the vibrational frequency initially increases with increasing pressure along the Hugoniot, but at higher pressures this trend is reversed. This reversal would indicate first a strengthening and then a weakening of the N_2 potential. Also, previous data analysis

indicates that higher vibrational states in N_2 are excited in <50 ns. and, within the limits of the approximations used and the experimental error, thermal equilibration of these levels is suggested.

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